Sign reversal of the 4f contribution to the hyperfine field at Sm in paramagnetic samarium compounds

S. K. Malik and R. Vijayaraghavan

Tata Institute of Fundamental Research, Homi Bhabha Road, Bombay 400005, India

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In paramagnetic rare-earth compounds, in the presence of an applied magnetic field, the 4f electrons produce a field at the rare-earth nuclear site, which, for the free Sm^{3+} ion, is positive at all temperatures. It is shown that because of crystal-field effects, the 4f contribution to the hyperfine field at Sm reverses its sign at one or two temperatures, unlike in the free ion. Exchange interaction between Sm^{3+} ions, in the presence of crystal fields, may induce or suppress the sign reversals in the hyperfine field.

I. INTRODUCTION

The study of magnetic susceptibility and the anomalous behavior of the Knight shift has evoked much current interest concerning the magnetic properties of Sm^{3+} ions in compounds containing samarium. In rare-earth intermetallic compounds the Knight shift K_f of the nonmagnetic constituent, arising from the exchange interaction between the conduction-electron spins and the rare-earth spins, is proportional to $\langle S_z \rangle_{av}$ of the rare-earth ion. For most of the rare earths $\langle S_z \rangle_{av}$ is proportional to the 4f susceptibility χ_f, so that a linear relation exists between K_f and χ_f. However, in the case of the Sm^{3+} ion, the energy separations between the lower multiplet levels are so small that temperature-independent Van Vleck terms,[1] associated with the second-order Zeeman effect, contribute appreciably both to the susceptibility and to the Knight shift, with the result that the linear relation between K_f and χ_f no longer holds. Further, White and Van Vleck[2] showed that in samarium compounds K_f should reverse sign at a temperature of about 300 K (called the crossover temperature).

The expected sign reversal of the Knight shift has been observed in $SmX^{3,4}$ (X = P, As, Sb, Bi), $SmAl_3$,[5] and $SmPt_2$.[6] However, the Knight shifts in $SmAl_2$,[7] $SmSn_3$,[6,8,9] and SmF_3[10] failed to show any crossover. We have shown earlier by a simple model[11,12] (later extended by Malik[13] and by de Wijn et al.[14]) that the crossover in the Knight shift may be suppressed because of the mixing of excited J levels of Sm^{3+} ion into the ground ($J = \frac{5}{2}$) level by crystal fields. This mixing of levels also considerably affects the magnetic moment on samarium in ferromagnetic samarium compounds.[15] In this paper we show that the 4f-induced hyperfine field at samarium in paramagnetic state is strongly influenced by crystal fields.

In paramagnetic rare-earth compounds, in the presence of an external magnetic field, the 4f electrons produce a field $\langle H_z^{4f} \rangle_{av}$ at the rare-earth nuclear site, which in the case of free Sm^{3+} ion[16,17] is *positive at all temperatures* (unlike $\langle S_z \rangle_{av}$) and does

not show any crossover, i.e., $\langle H_z^{4f} \rangle_{av}$ does not become zero (see Fig. 1, the curve marked free ion). However, we find that because of the mixing of J levels of Sm^{3+} by (cubic) crystal fields, the 4f contribution to the hyperfine field reverses its sign at some temperature, thus becoming negative at low temperatures. This is in striking contrast to the free-ion behavior. Two sign reversals may also occur in some cases. Further, we find that the exchange interaction between Sm^{3+} ions, in the presence of crystal fields, may also induce or suppress the sign reversals in $\langle H_z^{4f} \rangle_{av}$. (Here $\langle S_z \rangle_{av}$, $\langle H_z^{4f} \rangle_{av}$, etc. are Boltzmann averages of the expectation values of corresponding operators over the multiplet levels of the Sm^{3+} ion.)

II. THEORY AND CALCULATIONS

The contribution from the 4f electrons to the hyperfine field may be written in the operator form[18]

$$\vec{H}_{op}^{4f} = -2\mu_B \sum_i \{r_i^{-3}[\vec{l}_i - \vec{s}_i + 3\vec{r}_i(\vec{r}_i \cdot \vec{s}_i)/r_i^2]\} , \qquad (1)$$

where the summation is over all the 4f electrons. In order to calculate the average hyperfine field we need matrix elements of $\vec{H}_{op}^{4f}$ nondiagonal in J since crystal fields admix various J levels. The desired matrix elements can be obtained by first writing $\vec{H}_{op}^{4f}$ into tensorial form[19] and then using the standard techniques of tensor algebra.[18,20] This method requires the evaluation of $3-j$, $6-j$, and $9-j$ symbols and is quite cumbersome. However, for the Hund's-rule ground multiplet, closed-form expressions are available for the matrix elements of $\vec{H}_{op}^{4f}$. We note that $\vec{H}_{op}^{4f}$ is a vector, and by the Wigner-Eckart theorem its matrix elements in the JM representation are related to the matrix elements of the magnetic moment operator $(\vec{L} + 2\vec{S})$. Therefore, for the z component of the hyperfine-field operator, we can write

$$\langle SLJM | H_z^{4f} | SLJM \rangle = -2\mu_B \langle r^{-3} \rangle \langle J \| N \| J \rangle M , \qquad (2)$$

$$\langle SLJM | H_z^{4f} | SLJ - 1 M \rangle = -2\mu_B \langle r^{-3} \rangle$$

$$\times \langle J||N||J-1\rangle [J^2 - M^2]^{1/2} \, ,$$

$$(3)$$

where $\langle r^{-3}\rangle$ is the expectation value of the inverse

cube radius of the $4f$-electron orbital, and $\langle J||N||J\rangle$ and $\langle J||N||J-1\rangle$ are certain multiplicative factors which for the Hund's-rule ground multiplet are given by[16]

$$\langle J||N||J\rangle = \frac{J(J+1)+L(L+1)-S(S+1)}{2J(J+1)} + \nu \frac{g_s}{2} \left\{ 3J(J+1) - 2L(L+1) - 3S(S+1) \right.$$

$$\left. - \frac{[3J(J+1)-L(L+1)+S(S+1)][3J(J+1)-L(L+1)-3S(S+1)]}{4J(J+1)} \right\} \, , \qquad (4)$$

$$\langle J||N||J-1\rangle = -\left\{ 1 + \frac{\nu}{2}\frac{g_s}{2} [3J^2 - L(L+1) - 3S(S+1)] \right\} \left[\frac{[(S+L+1)^2 - J^2][J^2 - (S-L)^2]}{4J^2(2J+1)(2J-1)} \right]^{1/2} \, , \qquad (5)$$

with

$$\nu = \frac{4S - (2l+1)}{(2l-1)(2l+3)S(2L-1)} \qquad (6)$$

and $l = 3$ for f electrons. For trivalent rare-earth ions the values of $\langle J||N||J\rangle$ for the ground state and $\langle J||N||J-1\rangle$ between the ground state and the first excited state (with $g_s = 2$) have been tabulated by Elliott and Stevens.[21]

The cubic-crystal-field Hamiltonian with $\vec{z} || [001]$ axis of the cube is given by[22]

$$\mathcal{K}_C = A_4 \left[\sum_i (35z_i^4 - 30r_i^2 z_i^2 + 3r_i^4) + 5 \sum_i (x_i^4 - 6x_i^2 y_i^2 + y_i^4) \right]$$

$$+ A_6 \left[\sum_i (231z_i^6 - 315z_i^4 r_i^2 + 105z_i^2 r_i^4 - 5r_i^6) - 21 \sum_i (11z_i^2 - r_i^2)(x_i^4 - 6x_i^2 y_i^2 + y_i^4) \right] \, , \qquad (7)$$

with summation over all the $4f$ electrons. The matrix elements of $\mathcal{K}_C$ between states in the JM representation can be obtained either by the method of operator equivalents[21,23] (extended to elements nondiagonal in J) or by the methods of tensor algebra as outlined by Wybourne.[20] The procedure for calculating $\langle H_z^{4f}\rangle_{av}$ is the same as used earlier[11-14] for calculating $\langle S_z\rangle_{av}$ and $\langle L_z + 2S_z\rangle_{av}$. The Hamiltonian consisting of the spin-orbit term and the crystal-field terms,

$$\mathcal{K} = \lambda \vec{L} \cdot \vec{S} + \mathcal{K}_C \qquad (8)$$

is diagonalized within the lowest-three multiplet levels to obtain the energy eigenvalues $E_m^{(0)}$ and the eigenfunctions $|m\rangle$. In the paramagnetic state,

the exchange field H_{ex}, which the samarium ions exert on each other, is a fraction of the applied field H. Therefore, both the applied and the exchange fields may be treated as a perturbation over the Hamiltonian of Eq. (8). Thus, for $H || \vec{z}$ we find

$$\mathcal{K}_{pert} = \mu_B H(L_z + 2S_z) + 2\mu_B H_{ex} S_z \, , \qquad (9)$$

and in the molecular-field approximation the exchange field may be written as

$$2\mu_B H_{ex} = -\mathcal{J}_{ff}\langle S_z\rangle_{av} \, .$$

Calculating up to second order in perturbation theory the expectation value $\langle H_z^{4f}\rangle$ of each level and taking its Boltzmann average over all the levels, we get

$$\frac{\langle H_z^{4f}\rangle_{av}}{H} = \mu_B \left[\sigma_{L+2S, H^{4f}} - \mathcal{J}_{ff} \frac{\sigma_{L+2S, S}\, \sigma_{S, H^{4f}}}{1 + \mathcal{J}_{ff}\sigma_{S, S}} \right] \, , \qquad (10)$$

where the notation $\sigma_{A, B}$ is used for[14]

$$\sigma_{A, B} = \sigma_{B, A} = \sum_m \left[-\frac{\langle m|A_z|m\rangle\langle m|B_z|m\rangle}{kT} + 2 \sum_{m' \neq m} \frac{\langle m|A_z|m'\rangle\langle m'|B_z|m\rangle}{E_m^{(0)} - E_{m'}^{(0)}} \right] p_m^{(0)} \qquad (11)$$

with

$$p_m^{(0)} = \exp(-E_m^{(0)}/kT) \Big/ \sum_m \exp(-E_m^{(0)}/kT) \, .$$

In the calculations presented below the matrix elements of H_z^{4f} between $(J, J') = (\frac{5}{2}, \frac{5}{2})$, $(\frac{7}{2}, \frac{5}{2})$, $(\frac{7}{2}, \frac{7}{2})$, $(\frac{9}{2}, \frac{7}{2})$, and $(\frac{9}{2}, \frac{9}{2})$ have been included.
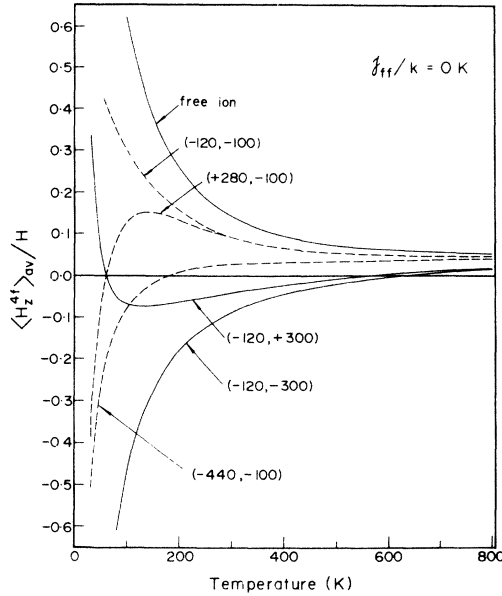
FIG. 1. Variation of $\langle H_z^{4f}\rangle_{av}/H$ as a function of temperature for few combinations of crystal-field parameters $A_4\langle r^4\rangle$ and $A_6\langle r^6\rangle$ in the absence of exchange. The numbers in parentheses are respectively, the values of $A_4\langle r^4\rangle/k$ and $A_6\langle r^6\rangle/k$ in kelvin.

III. RESULTS AND DISCUSSION

The results of the numerical calculations of the hyperfine field as a function of temperature for various combinations of the crystal-field param-
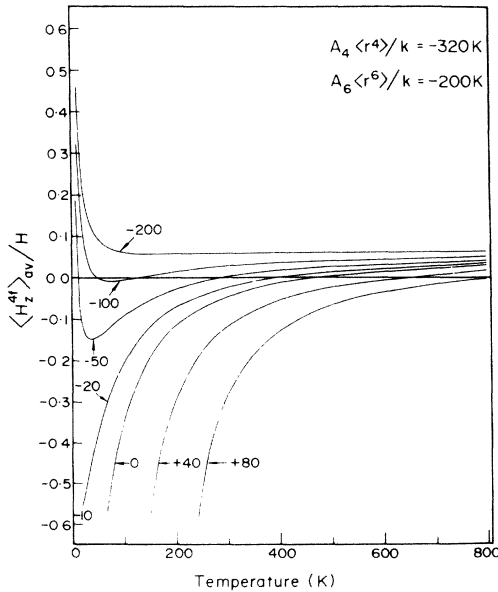

FIG. 2. Effect of exchange on the temperature dependence of $\langle H_z^{4f}\rangle_{av}/H$ with $A_4\langle r^4\rangle/k = -320$ K and $A_6\langle r^6\rangle/k = -200$ K. The curves are labeled with the values of $\mathcal{J}_{ff}/k$ in kelvin.

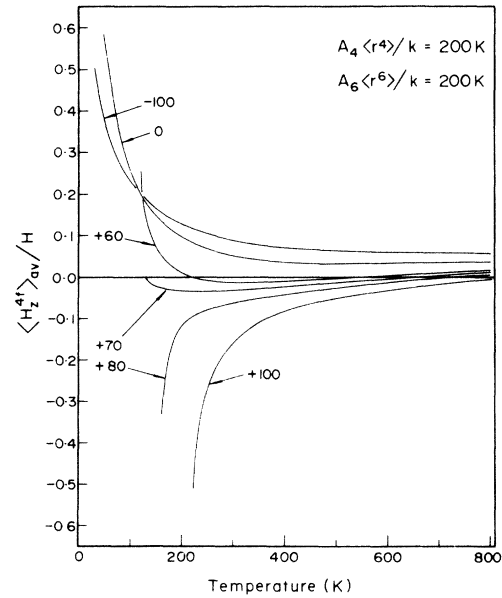FIG. 3. Effect of exchange on the temperature dependence of $\langle H_z^{4f}\rangle_{av}/H$ with $A_4\langle r^4\rangle/k = A_6\langle r^6\rangle/k = 200$ K. The curves are labeled with the values of $\mathcal{J}_{ff}/k$ in kelvin.

eters $A_4\langle r^4\rangle$, $A_6\langle r^6\rangle$, and the exchange constant $\mathcal{J}_{ff}$ are shown in Figs. 1–3. For $\langle r^{-3}\rangle$ the experimentally estimated value of Bleaney[24] has been used. In all the calculations the spin-orbit coupling has been taken to be $\lambda/k = 410$ K. In Fig. 1 we show the temperature dependence of $\langle H_z^{4f}\rangle_{av}/H$ for few typical values of $A_4\langle r^4\rangle$ and $A_6\langle r^6\rangle$ with $\mathcal{J}_{ff} = 0$. In the free-ion approximation $\langle H_z^{4f}\rangle_{av}/H$ is positive throughout. However, as the crystal-field strength increases, $\langle H_z^{4f}\rangle_{av}/H$ shows a sign reversal (or crossover) and becomes negative at low temperatures. For some combinations of $A_4\langle r^4\rangle$ and $A_6\langle r^6\rangle$ there are two sign reversals in $\langle H_z^{4f}\rangle_{av}/H$ and in this case it attains positive values at low temperatures as in the free-ion case. Different combinations of $A_4\langle r^4\rangle$ and $A_6\langle r^6\rangle$ may lead to identical crossover temperature, though the behavior may be different at intermediate temperatures. Thus we see that in the presence of crystal fields $\langle H_z^{4f}\rangle_{av}/H$ may show a variety of peculiar behaviors, with one, two, or no sign reversals. These results have an interesting consequence. One often measures the magnetic moment of nuclear excited states of samarium by measuring the product $\mu_{Sm}^{ex} H_{eff}$, where H_{eff} mainly consists of the $4f$-induced field and the applied field. (There are some other contributions which are much smaller than these two but must be taken into account while making comparison with experimental results.) Now if $\langle H_z^{4f}\rangle_{av}/H$ is negative (unlike in the free ion) and far exceeds unity, then not to mention the magnitude one may even end up with a wrong sign of the magnetic moment.

The effect of exchange interaction between samarium ions on $\langle H_z^{4f}\rangle_{av}/H$ in the presence of crystal fields is shown in Figs. 2 and 3. (An expression for $\langle H_z^{4f}\rangle_{av}/H$ for the free Sm^{3+} ion in the presence of applied and exchange fields is given in Ref. 25.) In Fig. 2, $A_4\langle r^4\rangle/k = -320$ K and $A_6\langle r^6\rangle/k = -200$ K and $\mathcal{J}_{ff}$ is varied. For $\mathcal{J}_{ff} = 0$ there is one crossover in $\langle H_z^{4f}\rangle_{av}/H$. For positive values of $\mathcal{J}_{ff}$ (ferromagnetic exchange) the crossover temperature increases as $\mathcal{J}_{ff}$ increases. For negative values of $\mathcal{J}_{ff}$ (antiferromagnetic exchange) the crossover temperature decreases as $|\mathcal{J}_{ff}|$ increases, then two crossovers appear and eventually for sufficiently large negative values of $\mathcal{J}_{ff}$ there is no crossover as in the free-ion case. In Fig. 3, the effect of exchange on the hyperfine field is shown for another set of crystal-field parameters namely, $A_4\langle r^4\rangle/k = A_6\langle r^6\rangle/k = 200$ K. For $\mathcal{J}_{ff} = 0$ there is no crossover in $\langle H_z^{4f}\rangle_{av}/H$. However it is to be noted that depending upon its strength a ferromagnetic exchange may induce one or two crossovers in $\langle H_z^{4f}\rangle_{av}/H$. Many of the curves in Fig. 3 pass through a point which corresponds to the temperature where $\langle S_z\rangle_{av}/H = 0$, so that $H_{ex} = 0$, and $\langle H_z^{4f}\rangle_{av}/H$ is independent of H_{ex}. Thus we see that

a strong ferromagnetic (antiferromagnetic) exchange interaction, in the presence of crystal fields, may induce (suppress) the crossover temperature(s) in $\langle H_z^{4f}\rangle_{av}/H$.

The quantity $\langle H_z^{4f}\rangle_{av}/H$ may also be termed as the $4f$ contribution to the Knight shift at the samarium nuclear site, but it is not the same as the $4f$ contribution to the Knight shift at the nonmagnetic constituents in samarium compounds. Unfortunately, nuclear magnetic resonance of samarium in the paramagnetic state has not been studied so far. However, nuclear techniques, such as perturbed angular correlation (PAC), can be used to measure the effective hyperfine field at the samarium nuclear site, in paramagnetic samarium compounds, in the presence of an externally applied magnetic field. Experiments using PAC technique are already underway[26] on samarium compounds (where crystal fields are known to be sizable) to study the effects reported in this paper, and preliminary results indicate that the $4f$-induced hyperfine field at samarium is indeed negative in one of the cubic compounds. Calculations of the hyperfine field on samarium in the ferromagnetic state will be presented in another paper.[27]

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over in $\langle H_z^{4f}\rangle_{av}$ for the free ion at about 700 K. This is incorrect, because while arriving at this result they considered only the direct contribution from $J=\frac{5}{2}$ state and the Van Vleck type contribution arising due to the mixing of $J=\frac{7}{2}$ state into $J=\frac{5}{2}$ state. However, at 700 K the direct contribution from $J=\frac{7}{2}$ and the Van Vleck type contribution from $J=\frac{5}{2}$ to $J=\frac{7}{2}$ states cannot be neglected. Inclusion of such contributions from all the multiplet levels produces only a shallow minimum in $\langle H_z^{4f}\rangle_{av}$ at about 900 K, but no sign reversal results. The proper calculation of $\langle H_z^{4f}\rangle_{av}$ for the free ion in the presence of an external field is given in Ref. 16, and the one in the presence of external and exchange fields in Ref. 25.

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